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Title

Electrochromic Element

BACKGROUND OF THE INVENTION

The invention concerns an electrochromic element with an electrochromic arrangement enclosed between two plane substrates, which arrangement comprises at least two electrode layers, one electrochromic layer, one ion storage layer, and one polymer electrolyte layer formed in situ, where the polymer electrolyte layer at the edge of the electrochromic element adjoins a sealing element.

Electrochromic elements of the aforementioned construction are known from numerous publications. They are employed inter alia for displays, dimmable mirrors, and glazing systems with variable light transmission. The plane substrates, which can be flat or also curved, consist in any case, in the case of large-area glazing systems, mostly of inorganic glass panes. They can also however consist of other materials, for example plastics. For the long-term stability of the electrochromic element it is indispensable for the substrates to be sufficiently impermeable to substances present in the environment, in particular to gases present in the ambient air. They must in addition reliably protect the electrochromic arrangement from migration of volatile constituents, such as for example plasticizers, solvents, etc. These requirements are particularly satisfactorily fulfilled by inorganic glass panes. For the sake of simplicity therefore, in the following text in connection with plane substrates, glass panes will principally be involved, without of course the invention being restricted thereto.

At least one of the electrode layers must be light-transmitting. Usually, one employs for both electrode layers transparent conductive metal oxide layers (TCOs), for example of ITO or doped tin oxide. The electrode layers have the purpose of permitting application to the electrochromic arrangement of an electric voltage, with which its light transmission can be varied. For the electrochromic layer it is usual to employ tungsten oxide-based materials, whose light transmission can be varied by embedding cations, such as H^+, Li^+, Na^+. As counterpart, the electrochromic layer requires an ion storage layer, also termed counter-electrode, for which numerous materials are known, including in particular cerium-titanium oxide and vanadium-titanium oxide.

The electrochromic layer and the ion storage layer are separated by an ion conduction layer ensuring ion transport between the two. Particularly for large-area electrochromic elements, the use of polymer electrolyte layers formed in situ has proved useful. The polymer electrolyte layers are formed by a liquid mixture containing inter alia monomers and at least one conduction salt being applied (injected) between the glass panes and being polymerized there. The polymer electrolyte layers can be present in the complete electrochromic element in solid, gel or also liquid form. They adjoin a sealing element at the edge of the electrochromic element.

The edge-side sealing element has primarily the function of sealing the electrochromic arrangement arranged between the glass panes also at the edge of the electrochromic element permanently against liquids and gases. In particular, it is necessary to prevent oxygen or water vapour present in the ambient air penetrating into the system. Within the scope of manufacture of the electrochromic element, the sealing element also performs the function of occluding the liquid monomer blend introduced between the glass panes in a liquid-impermeable manner. Such monomer blends frequently possess very low viscosity which may be below that of water, so that even minor leaks or pores in the sealing element would lead to undesirable escape of the monomer blend. Finally, the sealing element serves as a spacer between the glass panes, before the polymer electrolyte layer has hardened enough to assume this function itself.

From EP 0 836 932 A1, an electrochromic element with the features of the preamble is known, where a sealing element directly adjoins the polymer electrolyte layer, which sealing element consists of a liquid and gas-impermeable sealant which does not chemically react with the components of the electrochromic arrangement, in particular with the polymer electrolyte layer. As being suitable for this purpose, polyisobutylene-based butyl sealants are mentioned, these possessing an especially high level of impermeability to gas diffusion. The sealing element is not arranged between the glass panes, but adjoins a step formed by the glass panes and the electrochromic arrangement at the edge. With such an arrangement of the sealing element, production of the polymer electrolyte layer is rendered at least difficult. In addition, trials of the applicant have shown that sealing elements of butyl sealants during the course of polymerization of the polymer

electrolyte layer become detached from it at least locally, which can lead to premature ageing in these areas. In addition, it is extremely difficult to find a suitable sealant which is so readily compatible with the materials used for the polymer electrolyte layer that, even after a prolonged period of time, no material substitution or even a(n) (electro-) chemical reaction takes place between the two materials.

SUMMARY OF THE INVENTION

It is the object of the invention to configure electrochromic elements of the aforementioned construction so as to be permanently gas-impermeable, where undesirable interactions of the sealing element with the polymer electrolyte layer formed in situ or with other components of the electrochromic arrangement are to be prevented. Peeling of the sealing element off the polymer electrolyte layer during its polymerization should be prevented. The sealing element should, in addition, permit production of the electrochromic element, in particular introduction of the monomer blend necessary for formation of the polymer electrolyte layer, by customary production processes and reliably keep the plane substrates at a distance, at least during the production process.

This object is solved by an electrochromic element with the features of Claim 1. Advantageous configurations are the subject of the subclaims.

According to the invention, provision is made for the sealing element to consist of a plastically deformable liquid-impermeable adhesive strip of a polyacrylate directly contiguous to the polymer electrolyte layer and to the surfaces facing one another of the two plane substrates (glass panes), as well as of a sealing strand outwardly adjacent thereto consisting of a gas-impermeable sealant which is chemically compatible with the adhesive strip.

Surprisingly, it has proved successful, through the use of a sealing element according to the invention consisting of at least two separate functional components, to provide all the functions necessary for production and durable operation of an electrochromic element. Here, the adhesive strip primarily assumes the function of an edge closure for the polymer electrolyte layer, preventing escape of the liquid monomer blend, and in addition acts as a spacer for the glass panes.

By virtue of its plasticity, the adhesive strip can follow the polymer electrolyte layer contracting during the course of polymerization and does not peels off from it, as is the case with other known sealing elements. Polyacrylate materials are readily compatible with a series of materials used for the polymer electrolyte layers, in particular however with (meth)acrylic ester-based polymer electrolyte layers, which have proved especially suitable for this purpose.

The polyacrylate adhesive strip according to the invention is impermeable to liquid, but not however gas-impermeable. In particular, it is not sufficiently diffusion-impermeable to gases, such as oxygen and water vapour, and to solvents, such as propylene carbonate or ethylene carbonate. The adhesive strip is therefore, within the scope of the invention, supplemented functionally by a sealing strand of a highly gas-impermeable sealant which is chemically readily compatible with the adhesive strip.

It has been found that polyacrylate adhesive strips are especially suitable as a kind of resilient pad or adapter between the materials of the polymer electrolyte layer on the one hand and the sealants of the sealing strand on the other hand. The presence of such a resilient pad which is compatible with both materials permits the use of a wider variety of sealants than if they would adjoin directly the polymer electrolyte layer and would have to be (electro-) chemically compatible with it.

Preferably, the adhesive strip consists of adhesive tape, available in roll form, of a polyacrylate which possesses a glass transition temperature of less than 20 °C. Preferably, the glass transition temperature should be significantly below 20 °C, in particular below 10 °C.

Such adhesive tapes are for example manufactured and marketed under the commercial names Scotch Acrylic Foam or Scotch Isotact by Messrs 3M. Such adhesive tapes can be readily applied at room temperature. They adapt well to the shape of the adjacent surfaces and possess a type of self-healing effect, so that punctures which occur on penetration of the injection tools for insertion of the monomer blend between the glass panes quickly reclose of their own accord after removal of the tools. It is additionally recommended, when selecting the material of the adhesive

tape, that one should ensure that the material possesses a low to medium degree of crosslinking. This will ensure that the tackiness of the material is sufficiently high. The adhesive tape is applied prior to assembly of the components of the electrochromic element either manually or mechanically to the edges of the glass panes. Here, it is preferable to use a transparent adhesive tape. As the edge area of the electrochromic element is otherwise masked by the frame, it is also possible to use colored or opaque adhesive tapes.

Adhesive strips of polyacrylate whose water content is a maximum of 0,3 weight percent are especially suitable for durable functioning of the electrochromic elements. Preferably, the water content should be below 0.05 weight percent. If necessary, the adhesive strip should be subjected to suitable drying treatment prior to use. With a higher water content of the adhesive strip, there is the risk of diffusion of this water into the polymer electrolyte layer, which can lead to blistering and premature ageing.

The adhesive strip should preferably possess a width of at least 5 mm and a maximum of 20 mm. In the case of lesser widths, handling and achieving impermeability to liquid will be made difficult, whilst in the case of greater widths, the ratio of usable area to the overall area of the electrochromic element will be less favorable, without its properties being improved any further.

For the sealing strand, it is preferable to use a highly gas-impermeable butyl sealant of polyisobutylene or butyl rubber base, or an epoxy sealant.

Materials are preferred which, for prevention of leakage currents in the case of butyl sealants, possess a specific electrical conductivity of less than $10^{-9}\ \Omega^{-1}cm^{-1}$, preferably less than $10^{-11}\ \Omega^{-1}cm^{-1}$, and in the case of epoxy sealants a specific electrical conductivity of less than $10^{-12}\ \Omega^{-1}cm^{-1}$, preferably less than $10^{-13}\ \Omega^{-1}cm^{-1}$. In both cases, the water-vapour permeability in accordance with DIN 53122-1.2 (corresponding to prEN 1279-4) should be maximum approximately 4.0 $g \cdot m^{-2} \cdot d^{-1}$. The water-vapour permeability is determined in accordance with the Standard on 2 mm thick films from the corresponding material.

The aforementioned sealant materials are chemically especially compatible with the polyacrylate materials used for the adhesive strip according to the invention and possess excellent impermeability to diffusion in respect of gases such as oxygen and water vapour, as well as solvents such as for example polypropylene carbonate or ethylene carbonate. Other materials being common and well-known as sealants can also be used provided that they guarantee imperviousness to the gases stated comparable to the materials preferred within the scope of the invention and are compatible with the polyacrylate adhesive strips. This can be established by the specialist by means of simple tests.

Preferred butyl sealants are for example Bostik 5124 or 5125 (Messrs Bostik) with a butyl rubber base, possessing the following properties:

water-vapour permeability	approximately 0.10 - 0.15 $g \cdot m^{-2} \cdot d^{-1}$
specific electrical conductivity	approximately 10^{-11} $\Omega^{-1}cm^{-1}$

Preferred epoxy sealants are for example Araldit 2012 or 2014 (Ciba-Geigy) with the following properties:

water-vapour permeability	approximately 4.0 $g \cdot m^{-2} \cdot d^{-1}$
specific electrical conductivity	approximately 10^{-14} $\Omega^{-1}cm^{-1}$

or Eccobond 45 (Grace Specialty Polymers / Emerson & Cuming) with the following properties:

water-vapour permeability	approximately 2.5 $g \cdot m^{-2} \cdot d^{-1}$
specific electrical conductivity	approximately $3 \cdot 10^{-14}$ $\Omega^{-1}cm^{-1}$

Of course, a sealant, in particular with a base of butyl rubber, polyisobutylene or epoxy resin, functioning as edge seal of an electrochromic unit must be electrochemically inert in the electrical voltage range necessary for the function of the electrochromic element. This means that the

sealant may not evidence any electrochemical decomposition reactions on application of an electrical potential of, for example, 3 or 5 volts.

In addition of course, the sealing strand like the adhesive strip must be arranged along the entire pane edge between the glass panes in order to confine the electrochromic element jointly with the glass panes in a diffusion-impermeable manner. The sealing strand does not have to be flush with the pane edge. On the contrary, it can even overlap the pane edges, at least partially.

It can be advantageous if the electrochromic element is sealed towards the outside in known fashion with an additional sealant strand. Suitable for this purpose are in particular polysulfide-base materials used for double-glazing manufacture. This is especially appropriate if the electrochromic element is combined with at least one additional glass pane to form a double-glazing unit.

Preferably, the sealing strand adjoins directly the adhesive strip. It lies within the scope of the invention however to provide between the two components of the sealing element according to the invention at least one additional functional component, for example a separating layer or a primer layer, if the advantage achieved thereby is justified by the additional cost necessary. It is also possible for the glass panes in the region of the adhesive strip, the sealing strand or of an additional sealing strand to be provided with a primer in order to improve the adhesion of these materials to the glass.

The invention can be used to special advantage in the case of electrochromic elements with a polymer electrolyte layer which, in addition to the conduction salt necessary for provision of a sufficient quantity of cations (for example in accordance with WO 95-31 746 A1), incorporates at least one (meth)acrylic ester, at least one plasticizer and at least one polymerization initiator (EP 0 683 215 A1).

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is explained in further detail with the aid of the embodiments illustrated in the Figures. These show:

Figure 1 a first embodiment of the electrochromic element according to the invention in cross-section,

Figure 2 a second embodiment of the electrochromic element according to the invention in a similar representation.

The representation in the Figures is to be regarded as schematic. The dimensions are not to scale.

K DESCRIPTION OF THE PREFERED EMBODIMENT

The electrochromic element according to Figure 1 consists of two 4 mm thick transparent float glass panes 1 and 2 which are each provided on the surfaces facing one another with transparent electrode layers 3, 4 of indium-tin oxide (ITO), of fluorine-doped tin oxide or another electrically conductive metal oxide. On electrode layer 3 is arranged an electrochromic layer 5 of tungsten oxide, whilst on electrode layer 4 is located an ion storage layer 6 of one or more metal oxides, such as for example cerium, vanadium, titanium, zirconium or nickel oxide. The edge area of the electrode layers 3, 4 is in each case uncoated over an area of a few millimeters, as can be seen in the Figure. Not illustrated are the busbars by means of which an electrical voltage is applied to the electrode layers 3, 4.

Between the coated glass panes is located a 0.9 mm thick, in situ polymerized polymer electrolyte layer 7 in accordance with EP 0 683 215 A1 with a conduction salt content in accordance with WO 95-31 746 A1. It adjoins directly a 0.9 mm thick by 9 mm wide transparent adhesive strip 8 of a low-crosslinked polyacrylate, which has been formed from an adhesive tape of Messrs 3M with the corresponding dimensions marketed under the commercial name Scotch Isotac VHB 4910, which had been subjected to a drying treatment before application. The polyacrylate of this adhesive strip possesses a glass transition temperature of between 5 and 10°C. The glass transition temperature was determined by means of Dynamic Thermomechanometry (see for example "Examination Methods in Chemistry", Georg Thieme Verlag, 2nd impression 1990, Chapter 1, page 13).

The surrounding groove remaining between the outer surface of the adhesive strip 8 facing towards the edge of the electrochromic element and the outer edges of the glass panes 1, 2 is filled with a sealing strand 9 of an epoxy sealant Araldit 2012. The sealing strand 9 is essentially flush with the outer edges of the glass panes 1, 2. It could however at least partially overlap these edges.

Figure 2 shows in cross-section an edge view of a double-glazing unit formed with an electrochromic unit according to the invention. The embodiment of the electrochromic element according to Figure 2 differs from that of Figure 1 in that the glass pane 1 possesses smaller dimensions than glass pane 2. As in the previous example, an adhesive strip 8 formed of a Scotch Isotac VHB 4910 adhesive tape of Messrs 3M is provided, this adjoining directly the polymer electrolyte layer 7. The width of the adhesive strip 8 at 6 mm is in this case chosen to be slightly less than in the foregoing example, in order to compensate at least partly for the loss of available vision area which is caused by the stepped design of the electrochromic element. The adhesive strip 8 is adjoined in this case by a sealing strand 9 formed of a butyl sealant, Bostik 5125. The step formed by the two glass panes 1 and 2 and by the outer face of the sealing strand 9 is filled with a further sealant strand 10 of a polysulfide double-glazing adhesive, for example of a polysulfide Naftotherm M 82 of Messrs Chemetall. The sealant strand 10 is only illustrated in section, whilst all other components of the double-glazing unit, such as for example the spacer and the at least one other glass pane, have been omitted entirely. The construction of double-glazing units is generally known, so that it is unnecessary to illustrate further details in this context.

The two electrochromic elements illustrated in the Figures have withstood various ageing tests without discernible damage.